### PATENT ABSTRACTS OF JAPAN

(11)Publication number:

06-033295

(43)Date of publication of application: 08.02.1994

IDS(7)

(51)Int.Cl.

C25D 5/26 C25D 9/08

// C25D 3/66

(21)Application number: 04-188420

(71)Applicant: KAWASAKI STEEL CORP

(22) Date of filing:

15.07.1992

(72)Inventor: NAKAKOUJI NAOMASA

NAKAJIMA SEIJI GOMI SHUJI

MORITO NOBUYUKI

# (54) MANUFACTURE OF ZN-FE ALLOY COATED STEEL SHEET HAVING MGO LAYER ON SURFACE

(57)Abstract:

PURPOSE: To easily obtain a Zn-Fe alloy coated steel sheet excellent in corrosion resistance by executing cathodic electrolytic treatment to a steel sheet at a prescribed current density in molten salts essentially consisting of Mg salt and Zn salt and forming an MgO layer on the surface.

CONSTITUTION: The bath of the molten salts essentially consisting of Mg salt and Zn salt is prepd. In this molten salt bath, the steel sheet is subjected to cathodic electrolytic treatment at a high current density of >100 A/dm2 in the bath of the molten salts, and Zn is essentially precipitated to form a Zn–Fe alloy film. Next, it is subjected to cathodic electrolytic treatment at a low current density of < 50 A/dm2 in the same molten salt bath, and MgO is essentially precipitated. Then, the Zn–Fe alloy coated steel sheet having an MgO layer on the surface and excellent in corrosion resistance can be obtd.

### LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

### \* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

### **CLAIMS**

### [Claim(s)]

[Claim 1] Under the fused salt bath which makes magnesium salt and zinc salt a subject for a steel plate On the front face characterized by carrying out cathode electrolysis with the current density which exceeds 100 A/dm2, and subsequently carrying out cathode electrolysis with less than two 50 A/dm current density in this bath It has a MgO layer. The manufacture approach of a Zn-Fe alloy plate steel plate.

[Claim 2] Under the fused salt bath which makes zinc salt a subject for a steel plate On the front face characterized by electrolyzing with the current density which exceeds 100 A/dm2, and electrolyzing with less than two 50 A/dm current density in the fused salt bath which subsequently makes magnesium salt a subject It has a MgO layer. The manufacture approach of a Zn-Fe alloy plate steel plate.

[Translation done.]

### \* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]

[Industrial Application] This invention is on the front face excellent in the corrosion resistance used for an automobile car body, household electric appliances, building materials, etc. It has a MgO layer. It is related with the approach of manufacturing a Zn-Fe alloy plate steel plate for high productivity.

[0002]

[Description of the Prior Art] Although a galvanized steel sheet gives corrosion resistance to a steel plate using a sacrifice corrosion prevention operation of Zn, nickel, Fe, etc. are added in electric Zn system plating, aluminum etc. is further added by addition and melting Zn system plating and rust-proofing capacity is raised, since still sufficient corrosion resistance is not acquired, researches and developments of the galvanized steel sheet which has the corrosion resistance which was more excellent even in current are done.

[0003] Mg's being promising as an alloy element which raises the rust-proofing ability of Zn, and the thing of the engine performance which was excellent although the attempt of a Zn-Mg alloy plating was made are not yet made. The hot-dipping method was first inquired as the Zn-Mg alloy-plating approach, and it is JP,56-96036,A and Provisional Publication No. 56 No. -123359 official report, Provisional Publication No. 56 No. -125953 official report, Provisional Publication No. It is indicated by 56 No. ¬152956 official report etc. However, the melting point of Mg It is the melting point of Zn at 650 degrees C. Since little deer addition cannot be carried out at a melting Zn bath since it is far higher than 419 degrees C, but an alloy layer with high Fe concentration was moreover made to the interface of a plating layer and a steel plate and plating adhesion deteriorated, various alloying elements needed to be put in, and the material property deteriorated with heat, and the steel plate itself had problems, like workability worsens. [0004] It is based on vacuum deposition. Although the Zn-Mg alloy plating was proposed by JP.64-17851, A. JP.64-17852, A. and JP.64-17853, A. in vacuum deposition, there were problems. like the big heat source for evaporating a high degree of vacuum and high Mg, and Zn is required, and it is difficult for the top where cost is high for adhesion with a steel plate to obtain the precise and uniform plating layer which is not good. Since the single electrode potential of Zn and Mg is too different when the usual water solution is used in electroplating, it is very difficult to obtain an alloy plating. Provisional Publication No. In 58 No. -144492 official report, although the plating bath using a fluoride is shown, Mg content is obtained only for 1% or less of thing. [0005] Corrosion resistance is good like the above. It is difficult to obtain a Zn-Mg alloy-plating steel plate. Although the technique of having galvanized Zn in a lower layer and galvanizing Mg in the upper layer as what furthermore uses Mg was proposed by JP,62-109966,A, in order to cover Mg with vacuum deposition, high working costs were needed, and there was a problem also in the adhesion of Zn and Mg. It is difficult to use Mg as a metal as mentioned above. [0006] To these, it is Mg oxide as shown in JP,64-65253,A. Although the approach of covering with aluminum 203 and SiO2 is learned, it mainly aims at abrasion resistance. Since there are few MgO contents, corrosion resistance is inadequate, and there was a problem also in workability. Although JP,2-254178,A is known as what forms the compound coat which consists

of a metal Mg and its oxide on Zn system plating coat, in order to cover Metal Mg and Mg oxide with vacuum deposition, high working costs are needed, and corrosion resistance is [ adhesion with Zn system plating layer and Mg is bad, and there are few surface amounts of Mg oxides, and ] inadequate.

[0007] Then, this invention persons are already on a front face. It discovered that Zn system plating covering steel plate which has a MgO layer showed high corrosion resistance, and has applied as Japanese Patent Application No. No. 116733 [four to]. On the front face of Zn system plating The approach of cathode-electrolysis-processing or immersion processing using the fused salt bath which applies the solution containing a magnesium alkoxide compound as an approach of forming a MgO layer, and makes a heating art and magnesium salt a subject is suitable.

[8000]

[Problem(s) to be Solved by the Invention] However, the approach of carrying out cathode electrolysis processing using the fused salt bath which mainly contains magnesium salt and zinc salt among the approaches of forming a MgO layer and a Zn-Fe alloy layer Although the MgO layer could be formed in coincidence and it was convenient, it was what must carry out cathode electrolysis with two or less 50 A/dm current density for a long time, and is inferior to productivity by this approach.

[0009] This invention is on the front face which solved this trouble and was excellent in corrosion resistance with short-time cathode electrolysis processing. It has a MgO layer. It aims at offering the approach of manufacturing a Zn-Fe alloy plate steel plate.
[0010]

[Means for Solving the Problem] This invention is in the fused salt bath which makes magnesium salt and zinc salt a subject for a steel plate. It galvanizes with the current density which exceeds 100 A/dm2. Subsequently, it is the manufacture approach galvanized with less than two 50 A/dm current density in this bath. Under the fused salt bath which makes zinc salt a subject for a steel plate further again 100 A/dm2 It galvanizes with the current density which exceeds. On subsequently, the front face excellent in the corrosion resistance characterized by galvanizing magnesium salt with less than two 50 A/dm current density in the fused salt bath made into a subject It has a MgO layer. It is the manufacture approach of a Zn-Fe alloy plate steel plate. [0011]

[Function] If cathode electrolysis processing of the steel plate is carried out in the fused salt bath which makes magnesium salt a subject A MgO layer can be formed. It is not Metal Mg by cathode electrolysis processing. The reason MgO is formed is the moisture under fused salt bath, and OH, although it is not in \*\*. – What is depended on the oxidation by ion, oxygen or the moisture in an ambient atmosphere, and oxygen is presumed. Usually, magnesium salt contains moisture according to moisture absorption, and although electrolysis processing does not supply the moisture and OH– (moisture dissociates and arises in a fused salt bath) which oxidize Mg, and especially oxygen since it is performed in atmospheric air with moisture and oxygen, it can add a steam, the damp entrainment of oxygen, or a hydroxide suitably to a fused salt bath if needed.

[0012] If zinc salt is added to the fused salt which makes magnesium salt a subject, since Zn ion under bath will be returned to Metal Zn by cathode electrolysis, Zn plating is also formed in MgO and coincidence and whenever [ bath temperature ] Above 300 degrees C, it alloyed with heat. The alloy of Zn–Fe, and on it Since the steel plate which has a MgO layer is obtained, it is very convenient. However, when current density of cathode electrolysis processing is made high, only Zn is galvanized and it is required of this approach. Since the amount of MgO(s) could not be obtained, it was what is inferior to starting productivity for a long time having to electrolyze by the less than two 50 A/dm low current consistency, and obtaining the required amount of coats. [0013] In order to acquire the outstanding corrosion resistance, the amount of MgO(s) With two or more 0.1 g/m The amount of Zn–Fe alloy coats is required two or more 15 g/m, and it is electrolysis time amount about these amounts. High productivity cannot be attained if it is not made to form in a short time of 10 or less secs. As a result of examining various cathode electrolysis processing conditions in the fused salt bath which makes magnesium salt and zinc

salt a subject so that this invention persons may raise productivity, in order to have obtained the amount of coats required of a short time, it turned out that what is necessary is to electrolyze with high current density first and just to electrolyze by the low current consistency subsequently. By the alloying by the heat which Zn will mainly be galvanized if it electrolyzes with high current density, and advances to coincidence A Zn-Fe alloy coat is formed, required of a short time Current density for obtaining the amount of Zn-Fe 100 A/dm2 — exceeding desirable — Since a power-source facility will become huge and expensive if current density is made high too much, although it exceeds 200 A/dm2 and it comes out, it is, and productivity becomes high so that current density is high It is desirable to make it less than two 500 A/dm. [0014] If it electrolyzes by the low current consistency, it is to the Lord. MgO is formed. It is required. When 50 A/dm2 is exceeded, the rate of current density for obtaining the amount of MgO(s) that Zn is galvanized increases, and it is required of less than two 50 A/dm. The amount of MgO(s) is not obtained. It is required when current density is too low. Since it comes to take long duration to obtain the amount of MgO(s), it is desirable not to make it less than two 5 A/dm. Although high current density electrolysis and low current consistency electrolysis should just perform magnesium salt and zinc salt continuously by the same fused salt bath made into a subject, they are separately good in a line respectively at the fused salt bath which makes magnesium salt a subject for low current consistency electrolysis again by the fused salt bath which makes zinc salt a subject for high current density electrolysis.

[0015] As for magnesium salt and zinc salt, the magnesium chloride and the zinc chloride are most suitable in respect of a price, the melting point, and handling, respectively. It is desirable to use a sodium chloride, potassium chloride, a lithium chloride, etc. for a fused salt bath as a melting-point-lowering agent and an electrical conduction assistant in addition to these salts, the temperature of a fused salt bath — alloying of Zn — and — From the point of MgO formation 300 degrees C or more — desirable — more — desirable — It is 400 degrees C or more. Since the steam of a zinc chloride not only comes to occur, but the quality of the material of a steel plate will deteriorate if the temperature of a fused salt bath is too high It is desirable to make it 500 degrees C or less.

[0016]

[Example] The example and the example of a comparison of this invention are explained below. Cathode electrolysis is performed on the conditions which carry out the preheating of the cold rolled sheet steel to plating temperature, and show it in Table 1 in the fused salt bath of following A-D after carrying out acid washing, the usual cleaning and, and it is on a front face. It has a MgO layer. The Zn-Fe alloy coat steel plate was produced.
[0017]

[Fused salt bath A]

MgCl2 8mol%ZnCl2 52mol%NaCl 20mol%KCl 20-mol% [the fused salt bath B]

MgCl2 10mol%ZnCl2 56mol%NaCl 28mol%KCl Six-mol% [the fused salt bath C]

ZnCl2 60mol%NaCl 20mol%KCl 20-mol% [the fused salt bath D]

MgCl2 60mol%NaCl 20mol%KCl 20-mol% [0018]

[Table 1]

	高電流密度電解				低電流密度電解				被膜量		赤錦発生 日数 *
	浴	温度(℃)	電流密度 (A/du²)	時間 (sec)	浴	温 度 (℃)	電流密度 (A/dm²)	時間 (sec)	Mg() (g/m²)	ZnFe (g/m²)	(日)
実施例1	Α	450	200	4.5	A	450	15	4.0	2.2	20.0	40
実施例2	Α	420	400	3.4	A	420	10	3.0	1.7	30.0	38
実施例3	В	400	300	5.0	В	400	20	5.0	2.0	27.0	45
実施例4	В	470	500	4.6	В	470	10	5.0	3.0	45.0	55
実施例5	С	350	150	5.0	D	450	15	3.0	1.9	24.0	43
実施例6	С	400	250	5.1	D	480	20	5.0	5.3	32.0	50
実施例7	Α	440	500	2.0	D	430	45	5.0	2.5	25.0	44
比较例 1	_	_			Α	440	20	64.0	4.3	20.0	42
<b>共發例</b> 2	В	400	200	12.8	_				0	28.0	2
进续例3	С	350	_20_	6.0	D	400	_100	4.0	0.1	2.0	1
比較初 4	A	440	<u>75</u>	3.0	Α	440	_300	6.0	0 .	6.0	1

\*) 赤錆発生日は塩水噴霧試験(JIS Z 2371)により求めた。

[0019] The corrosion-resistant ability of each steel plate was also collectively shown in Table 1. On the front face which was excellent in corrosion resistance short-time electrolysis by the manufacture approach of this invention so that clearly from Table 1 It has a MgO layer. It turns out that a Zn-Fe alloy coat steel plate can be manufactured. [0020]

[Effect of the Invention] It is in the fused salt bath to which this invention makes magnesium salt and zinc salt a subject for a steel plate as explained above. On the front face which was excellent in corrosion resistance with high productivity since it galvanized with the current density which exceeds 100 A/dm2 and subsequently galvanized with less than two 50 A/dm current density in this bath The Zn-Fe alloy plate steel plate which has a MgO layer can be manufactured, and the industrial value is very large.

[Translation done.]

<sup>※)</sup>実線のアンダーラインは本発明の請求範囲外であることを示し、点線のアンダーラインは長時間**逆**解で生産性に劣ることを示す。

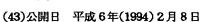
### (19)日本国特許庁(JP)

### (12) 公開特許公報(A)

庁内整理番号

(11)特許出願公開番号

## 特開平6-33295



(51)Int.Cl.5 -

識別記号

F

FΙ

技術表示箇所

C 2 5 D 5/26

9/08

// C25D 3/66

審査請求 未請求 請求項の数2(全 4 頁)

(21)出願番号

特願平4-188420

(71)出願人 000001258

川崎製鉄株式会社

(22)出願日

平成 4年(1992) 7月15日

兵庫県神戸市中央区北本町通1丁目1番28

(72)発明者 中小路 尚匡

千葉県千葉市中央区川崎町1番地 川崎製

鉄株式会社技術研究本部内

(72)発明者 中島 清次

千葉県千葉市中央区川崎町1番地 川崎製

**鉄株式会社技術研究本部内** 

(74)代理人 弁理士 小林 英一

最終頁に続く

(54) 【発明の名称】 表面にMg O層を有するZn-Fe合金被覆鋼板の製造方法

### (57)【要約】

【目的】 マグネシウム塩と亜鉛塩を主として含有する 溶融塩浴を用いて、短時間の陰極電解処理で耐食性に優 れた表面に MgO層を有する Zn-Fe合金被覆鋼板を製造す ることのできる方法を提案する。

【構成】 鋼板をマグネシウム塩と亜鉛塩を主体とする 溶融塩浴中で 100A /dm 超えの電流密度でめっきし、次 いで同浴中で50A/dm²未満の電流密度でめっきする。

1

### 【特許請求の範囲】

【請求項1】 鋼板をマグネシウム塩と亜鉛塩を主体とする溶融塩浴中で 100A/cm² 超えの電流密度で陰極電解し、次いで同浴中で50A/cm² 未満の電流密度で陰極電解することを特徴とする表面に MgO層を有する Zn-Fe合金被覆鋼板の製造方法。

【請求項2】 鋼板を亜鉛塩を主体とする溶融塩浴中で 100A/dm 超えの電流密度で電解し、次いでマグネシウム塩を主体とする溶融塩浴中で50A/dm 未満の電流密度 で電解することを特徴とする表面に MgO層を有する Zn- 10 Fe合金被覆鋼板の製造方法。

### 【発明の詳細な説明】

[0001]

【産業上の利用分野】本発明は、自動車車体、家電、建材等に用いられる耐食性に優れた表面に McO層を有する Zn-Fe合金被覆鋼板を高い生産性で製造する方法に関するものである。

【従来の技術】亜鉛めっき鋼板はZnの犠牲防食作用を利用して鋼板に耐食性を持たせたものであり、更に電気Zn 20

[0002]

系めっきではNi、Feなどを添加、溶融Zn系めっきではAlなどを添加して防錆能力を向上させているが、まだ充分な耐食性が得られていないので現在でもより優れた耐食性を有する亜鉛めっき鋼板の研究開発が行われている。【0003】MgはZnの防錆能を向上させる合金元素として有望であり、 Zn-Mg合金めっきの試みがなされているが優れた性能のものは未だ出来ていない。 Zn-Mg合金めっき方法として最初に検討されたのは溶融めっき法であり、特開昭56-96036号公報、特開昭56-123359号公報、特開昭56-125953号公報、特開昭56-152956号公報等に 30記載されている。しかしMgの融点は650℃でZnの融点419℃よりはるかに高いために溶融Zn浴には少量しか添加できず、しかもめっき層と鋼板の界面にFe濃度の高い合

金層ができてめっき密着性が劣化するために色々な添加

元素を入れる必要があり、また鋼板自体も熱で材料特性

が劣化して加工性が悪くなる等の問題があった。

【0004】蒸着法による Zn-Mg合金めっきが特開昭64-17851号公報、特開昭64-17852号公報、特開昭64-17853号公報で提案されているが、蒸着法では高い真空度とMg、 Znを蒸発させるための大きな熱源が必要でコストが高いうえに、鋼板との密着性が良くなく、また緻密で均一なめっき層を得ることが難しい等の問題があった。電気めっき法では通常の水溶液を使用するとZnとMgの単極電位が違いすぎるために合金めっきを得ることが極めて難しい。特開昭 58-144492号公報ではフッ化物を使うめっき浴が示されているがMg含有量が1%以下のものしか得られていない。

【0005】以上のごとく耐食性の良い Zn-Mg合金めっき鋼板を得ることは困難である。さらにMgを利用するものとして下層にZn. 上層にMgをめっきする技術が特開昭 50

2

62-109966号公報に提案されているが、蒸着法でMgを被 覆するために高い生産費を必要とし、またZnとMgとの密 着性にも問題があった。以上のようにMgを金属として利 用するのは困難である。

【0006】 これらに対し、特開昭64-65253号公報に示されているようにMc酸化物を Al, Q やSiQ と共に被覆する方法が知られているが、主に耐摩耗性を目的としたものであり MgO含有量が少ないので耐食性が不十分であり、また加工性にも問題があった。 Zn系めっき皮膜上に金属Mg及びその酸化物からなる複合被膜を形成しているものとして特開平2-254178号公報が知られているが、蒸着法で金属MgとMc酸化物を被覆するために高い生産費を必要とし、またZn系めっき層とMgとの密着が悪くかつ表面のMc酸化物量が少なく耐食性が不十分である。

【0007】そこで、本発明者らは既に表面に MgO層を有するZn系めっき被覆鋼板が高耐食性を示すことを発見し、特願平4-116733号として出願している。Zn系めっきの表面に MgO層を形成する方法としては、マグネシウムアルコキシド化合物を含有する溶液を塗布し加熱処理方法やマグネシウム塩を主体とする溶融塩浴を用い陰極電解処理または浸漬処理する方法が適している。

[0008]

【発明が解決しようとする課題】しかしながら、 MqO層を形成する方法のうち、マグネシウム塩と亜鉛塩を主として含有する溶融塩浴を用いて陰極電解処理する方法は、 Zn-Fe合金層と MgO層を同時に形成することができて好都合であるが、この方法では50A/dm²以下の電流密度で長時間陰極電解しなければならず生産性に劣るものであった。

【0009】本発明は、この問題点を解決し、短時間の 陰極電解処理で耐食性に優れた表面に MgO層を有する Z n-Fe合金被覆鋼板を製造する方法を提供することを目的 とするものである。

[0010]

[0011]

【作用】マグネシウム塩を主体とする溶融塩浴中で鋼板を陰極電解処理すれば MgO層を形成することができる。 陰極電解処理によって金属Mgではなくて MgOが形成される理由は明かではないが、溶融塩浴中の水分、OH イオン、酸素あるいは雰囲気中の水分、酸素による酸化作用によるものと推定される。通常マグネシウム塩は吸湿に 3

より水分を含んでおり、かつ電解処理は水分、酸素のある大気中で行われるのでMgを酸化させる水分、OF(水分が溶融塩浴中で解離して生じる)、酸素を特に供給することはないが、必要に応じて溶融塩浴に水蒸気や湿った酸素の吹き込み、あるいは水酸化物等の添加を適宜行うことができる。

【0012】マグネシウム塩を主体とする溶融塩に亜鉛塩を添加すると、浴中のZnイオンが陰極電解により金属Znに還元されるので、MgOと同時にZnめっきも形成され、浴温度が300℃以上では熱で合金化したZn-Feの合10金とその上にMgO層を有する鋼板が得られるので非常に好都合である。しかしながらこの方法では陰極電解処理の電流密度を高くするとZnばかりめっきされ必要なMgO量を得ることができないので、50A/dm²未満の低電流密度で電解しなければならず必要な被膜量を得るのに長時間かかり生産性に劣るものであった。

【0013】優れた耐食性を得るには、MgO量が 0.1g/m以上で Zn-Fe合金被膜量が15g/m以上必要であり、とれらの量を電解時間 10sec以下の短時間で形成させなければ高い生産性を達成することはできない。本発明者ら 20は生産性を向上させるべくマグネシウム塩と亜鉛塩を主体とする溶融塩浴での陰極電解処理条件を種々検討した結果、短時間で必要な被膜量を得るには、まず高電流密度で電解し、次いで低電流密度で電解すればよいことが分かった。高電流密度で電解すると主にZnがめっきされ、同時に進行する熱による合金化で Zn-Fe合金被膜が形成される。短時間で必要な Zn-Fe型を得るための電流密度は 100A/dm 超え、望ましくは 200A/dm 超えであり、電流密度は高いほど生産性は高くなるが電流密度を高くしすぎると電源設備が巨大かつ高価になるので 500 30 A/dm 未満にしておくことが望ましい。

【0014】低電流密度で電解すると主に MgOが形成される。必要な MgO量を得るための電流密度は50A/dm<sup>2</sup>未満で、50A/dm<sup>2</sup>を超えるとZnがめっきされる割合が多くなり必要な MgO量が得られない。電流密度が低過ぎると必要な MgO量を得るのに長時間を要するようになるので5A/dm<sup>2</sup>未満にしないことが望ましい。高電流密度電解と低電流密度電解はマグネシウム塩と亜鉛塩を主体とする同じ溶融塩浴で続けて行えば良いが、高電流密度電解を亜鉛塩を主体とする溶融塩浴でまた低電流密度電解を40

マグネシウム塩を主体とする溶融塩浴でそれぞれ別々に 行っても良い。

【0015】マグネシウム塩、亜鉛塩は価格、融点、取扱の点でそれぞれ塩化マグネシウム、塩化亜鉛が最も適している。溶融塩浴にはこれらの塩以外に塩化ナトリウム、塩化カリウム、塩化リチウム等を融点降下剤、電導助剤として用いることが好ましい。溶融塩浴の温度はZnの合金化および MoO形成の点から 300℃以上が好ましく、より好ましくは 400℃以上である。溶融塩浴の温度は高過ぎると塩化亜鉛の蒸気が発生するようになるばかりでなく鋼板の材質が劣化するので 500℃以下にしておくことが望ましい。

### [0016]

【実施例】本発明の実施例および比較例を以下に説明する。冷延鋼板を通常の脱脂、酸洗したのちめっき温度まで予熱し、下記のA~Dの溶融塩浴中で表1に示す条件で陰極電解を行い、表面に Mapo層を有する Zn-Fe合金被膜鋼板を作製した。

### [0017]

### [溶融塩浴A]

 MgCl<sub>2</sub>
 8 mol%

 ZnCl<sub>2</sub>
 52mol%

 NaCl
 20mol%

 KCl
 20mol%

#### 「溶融塩浴B]

 MgCl<sub>2</sub>
 10mol%

 ZnCl<sub>2</sub>
 56mol%

 NaCl
 28mol%

 KCl
 6 mol%

### 「溶融塩浴C]

ZnC12

NaCl 20mol% KCl 20mol% [溶融塩浴 D]

60mo1%

MgCl<sub>2</sub> 60mol% NaCl 20mol%

KC1 20mo1%

[0018]

【表1】

		*									
	高電流密度電解				低電流密度電解				被膜量		赤錦発生 日数 •
	裕	温 度 (T)	電流密度 (A/du²)	時間 (sec)	浴	温度(丁)	電流密度 (A/du²)	時間 (sec)	MgO (g/m²)	ZnFe (g/m²)	(日)
実施例 1	Α	450	200	4.5	Α	450	15	4.0	2.2	20.0	40
実施例2	Α	420	400	3.4	A	420	10	3.0	1.7	30.0	38
実施例3	В	400	300	5.0	В	400	20	5.0	2.0	27.0	45
実施例 4	В	470	500	4.6	В	470	10	5.0	3.0	45.0	55
実施例5	С	350	150	5.0	D	450	15	3.0	1.9	24.0	43
実施例6	С	400	250	5.1	D	480	20	5.0	5.3	32.0	50
実施例7	A	440	500	2.0	D	430	45	5.0	2.5	25.0	44
比較例 I		_			Α	440	20	64.0	4.3	20.0	42
<b>比較例</b> 2	В	400	200	12.8	_			. —	0	28.0	2
比較例3	С	350	_20_	6.0	D	400	_100	4.0	0.1	2.0	1
HARRIN 4	A	440	<u>75</u>	3.0	A	440	_300	6.0	0	6.0	1

- \*)赤緒発生日は塩水噴霧試験(JIS Z 2371)により求めた。 ※)実線のアンダーラインは本発明の請求節囲外であることを示し、点線のアンダーラインは長時間電解で生産 性に劣ることを示す。

【0019】各鋼板の耐食性能も表1に併せて示した。 表1から明らかなように、本発明の製造方法では短時間 の電解で耐食性に優れた表面に MgO層を有する Zn-Fe合 金被膜鋼板が製造できることが分かる。

[0020]

【発明の効果】以上説明したように、本発明は鋼板をマ\*

\* グネシウム塩と亜鉛塩を主体とする溶融塩浴中で 100A /dm<sup>2</sup>超えの電流密度でめっきし、次いで同浴中で50A/d m 未満の電流密度でめっきするので高い生産性で耐食性 に優れた表面に MgO層を有するZn-Fe合金被覆鋼板を製 造することができ、その工業的価値は大変大きいもので ある。

フロントページの続き

(72)発明者 五味 修二

千葉県千葉市中央区川崎町1番地 川崎製 鉄株式会社技術研究本部内

(72)発明者 森戸 延行

千葉県千葉市中央区川崎町1番地 川崎製 鉄株式会社技術研究本部内